Development of Direct Generation of Carbon-centered Radicals via Cleavage of C-H Bond and Their Reactions

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During our study on development of a catalytic asymmetric addition reaction of dimethylzinc to imines, we accidentally found an addition reaction of the solvent, THF to the imine. This reaction was found to be a radical reaction caused by methyl radical generated by the reaction of dimethylzinc with air oxygen. Most of the methods widely used for the generation of carbon-centered radicals are based on a homolytic cleavage of carbon-heteroatom bonds. The significance of this reaction lies in the direct generation of a carbon-centered radical by the cleavage of a carbon-hydrogen bond. Using this dimethylzinc initiator, carbon-centered radicals can be directly generated directly from ethers and also from nonfuctionalized cycloalkanes. We developed reactions of directly generated ether radicals with C=N, C=O, and C=C bonds as well as amine functionalities. Recently, we have succeeded in development of an asymmetric version of the ether radical addition. The addition products of 4,4,5,5-tetramethyl-1,3-dioxolane to chiral *N*-sulfinyl imines were obtained in good yield with high stereoselectivity. The products can be easily converted into the corresponding chiral amino alcohols.